

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
30 September 2004 (30.09.2004)

PCT

(10) International Publication Number

WO 2004/083131 A1

- (51) International Patent Classification⁷: C02F 5/14 (81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (21) International Application Number:
PCT/GB2004/001150
- (22) International Filing Date: 18 March 2004 (18.03.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
0306531.5 21 March 2003 (21.03.2003) GB
- (71) Applicant (*for all designated States except US*): RHODIA CONSUMER SPECIALTIES LIMITED [GB/GB]; Oak House, Reeds Crescent, Watford, Hertfordshire WD24 4QP (GB).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): JONES, Christopher, Raymond [GB/GB]; 110 Sutherland Road, Cheltenham Hay, Nr. Walsall, South Staffordshire WS6 7BS (GB). GRECH, Jason, Mark [GB/GB]; 24 Bamburgh Crescent, The Berkeleys, Worcester WR4 0QX (GB).
- (74) Agent: BARKER BRETTELL; 138 Hagley Road, Edgbaston, Birmingham B16 9PW (GB).
- (84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2004/083131 A1

(54) Title: FORMULATION FOR CORROSION AND SCALE INHIBITION

(57) Abstract: A formulation comprising a THP⁺ salt and a thio-substituted compound. The formulation is suitable for use in the treatment of corrosion and metal sulphide scale deposits in aqueous systems. The thio-substituted compound may be a thio-substituted carboxylic acid or salt, a thio-substituted sulphonic acid, a substituted or unsubstituted alkyl or aryl thiol, a thio-substituted heterocyclic compound or a mercaptoethanol.

JC17 Rec'd PCT/PTO 20 SEP 2005

FORMULATION FOR CORROSION AND SCALE INHIBITION

The present invention relates to a method of preventing or alleviating the problems associated with metal sulphide deposits and to novel 5 formulations for use in such a method.

Tetrakis (hydroxyorgano) phosphonium salts (hereinafter THP⁺ salts), especially tetrakis (hydroxymethyl) phosphonium sulphate (hereinafter THPS) are widely used as metal sulphide dissolver/dispersers within 10 aqueous systems and especially those systems associated with oilfields.

When THPS is used in oilfields, it is typically applied in concentrations of up to 30%, together with an ammonium salt to improve performance. This combination of THPS and an ammonium salt, together with high 15 temperatures that can be experienced in oilfield applications, can be corrosive to mild steel and other metal components.

It is an aim of the present invention to ameliorate the above problems of corrosion by THP⁺ salts when used in aqueous systems.

20 Accordingly, the present invention, in a first aspect, provides a formulation for use in the treatment of corrosion and metal sulphide scale deposits in aqueous systems, said formulation comprising a THP⁺ salt (as hereinbefore defined) and a thio-substituted compound.

25 The metal sulphide scale may be iron sulphide. Alternatively, the metal sulphide may be lead sulphide or zinc sulphide or a combination thereof. The iron sulphide may be Troilite (FeS) or Pyrite (FeS₂). Alternatively, the iron sulphide may be Mackinawite (Fe₃S₈) or Phyrrhotite (Fe₃S₈).

30

The anion of the THP⁺ salt should be compatible with the aqueous system. Preferred anions include sulphate, chloride, phosphate, bromide, fluoride, carbonate, citrate, lactate, tartrate, borate, silicate, formate and acetate. The anion should make the THP⁺ salt water-soluble.

5

The thio-substituted compound is preferably thioglycollic acid (CAS No 68-11-1). Alternatively, the thio-substituted compound is selected from the group consisting of thio-substituted carboxylic acids or salts e.g. thiolactic acid, thiomalic acid and mercaptopyruvic acid; thio-substituted sulphonic acids e.g. mercaptoethane sulphonic acid; mercaptoalcohols e.g. mercaptoethanol; alkyl or aryl thiols (substituted and unsubstituted) e.g. mercaptoethane and thiocresol; and thio-substituted heterocyclic compounds e.g. mercaptomethylimidazole, mercaptothiazoline and mercaptopyridine.

15

The formulation may further include a surfactant. The surfactant is preferably a cationic surfactant, for example quaternary ammonium compounds, N-alkylated heterocyclic compounds or quaternised amido-amines. Anionic, amphoteric or non-ionic surfactants may also be used.

20 The use of ammonium salts may be substituted for an aminomethane phosphonate.

The formulation according to the invention is particularly useful in the prevention of corrosion of mild steel, copper and aluminium.

25

The present invention also provides, in a second aspect, a method for treatment of an aqueous system containing or in contact with a metal sulphide scale while concomitantly inhibiting the corrosion of surfaces in contact with said aqueous system, which method comprises the addition to 30 said aqueous system of a scale and corrosion inhibiting amount of a formulation in accordance with the first aspect of the invention.

The aqueous system is preferably one used in enhanced oil recovery. Alternatively, the aqueous system is one used in industrial water systems, paper manufacturing systems and any aqueous system wherein corrosion 5 caused by THP⁺ salts occurs.

The present invention also provides, in a third aspect, a formulation consisting essentially of the reaction product of a THP⁺ salt a thio-substituted compound, wherein the ratio of said THP⁺ salt and said 10 thio-substituted compound is between 1:1 and 750:1.

The formulation as described in the first aspect is preferably used in an effective amount up to 30% by weight as THP⁺. The amount used will vary by application but it may also be effectively used for low level 15 applications e.g. 1 to 10000ppm as a THP⁺ salt or in high level applications as 1 to 30% as a THP⁺ salt. In the second aspect THP⁺ is preferably used in an effective amount of up to 30% by weight as a THP⁺ salt with the co-addition of a thio-substituted compound in an effective amount of between 0.1 to 10000 ppm in relation to the volume of the 20 system being treated.

The ratio of THP⁺ to the thio-substituted compound in the formulation is typically in the range 1:1 to 750:1, more preferentially 15:1 to 300:1, most preferably 75:1 to 150:1.

25

The present invention will be illustrated, merely by way of example, as follows.

Example 1.

30 **Blank Experiment:** A 100ml solution of 20% THPS (26.6g TOLCIDE® PS75) and 1g ammonium chloride in synthetic seawater was placed in a

120ml screw-top jar. A pre-weighed mild steel coupon was immersed in the solution. The jar was then stored in a 50°C oven for 48 hours. After this time the coupon was cleaned by gentle scrubbing in water, washed with acetone and dried in the oven. The coupons were then reweighed and 5 the corrosion rate calculated according to the equation:

$$\text{Rate} = \frac{K \times W}{A \times T \times d}$$

10 W = Weight loss in g (to 0.1mg)

A = Area in Cm² (to 0.01 cm²)

T = Time of exposure in hours

d = Density in g/cm³

15 K is a constant defined by the units in which the corrosion rate is required. For example:

<u>Units</u>	<u>K</u>
Mpy - mils per year	3.45 x 10 ⁶

20

This experiment was repeated with various levels of corrosion inhibitor added to the blank solution. The results are shown in the table below:

TABLE

Experiment	Corrosion Rate mpy
Blank	208
Blank + 5000ppm Inhibitor A	77
Blank + 5000ppm Inhibitor B	197
Blank + 5000ppm Inhibitor C	116
Blank + 5000ppm Inhibitor D	132
Blank + 5000ppm Inhibitor E	88
Blank + 5000ppm Inhibitor F	86
Blank + 5000ppm Inhibitor G	28
Blank + 1% Inhibitor E	78
Blank + 1% Inhibitor F	74
Blank + 1% Inhibitor G	14
Blank + 100ppm Thioglycollic acid	47
Blank + 1000ppm Thioglycollic acid	38
Blank + 1000ppm Thioglycollic acid + 1000ppm quaternary ammonium chloride	23
Blank + 2800ppm Thioglycollic acid + 1000ppm quaternary ammonium chloride	17

Blank - A solution consisting of 20% THPS and 1% ammonium chloride in synthetic seawater.

Inhibitor A - Commercially available corrosion inhibitor comprising ethoxylated ammonium chloride, dibutyl thiourea and ethoxylated fatty acid.

Inhibitor B - Commercially available corrosion inhibitor comprising polyoxyethylene 2-ethylhexyl ether phosphate.

Inhibitor C - Oilfield corrosion inhibitor comprising fatty acids and Tall oil reaction products with diethylene triamine.

5 **Inhibitor D** - Commercially available corrosion inhibitor comprising a phosphonocarboxylic acid.

Inhibitor E - Standard commercially available oilfield corrosion inhibitor based on an amine alkoxylate.

10 **Inhibitor F** - Standard commercially available oilfield corrosion inhibitor comprising an amine ethoxylate and a quaternary ammonium chloride.

Inhibitor G - Standard commercially available oilfield corrosion inhibitor comprising thioglycollic acid and a quaternary ammonium chloride.

CLAIMS

1. A formulation for use in the treatment of corrosion and metal sulphide scale deposits in aqueous systems, said formulation comprising a
5 THP⁺ salt (as hereinbefore defined) and a thio-substituted compound.
2. A formulation as claimed in Claim 1 in which the metal sulphide scale is iron sulphide.
- 10 3. A formulation as claimed in Claim 1 in which the metal sulphide scale is lead sulphide.
4. A formulation as claimed in Claim 1 in which the metal sulphide scale is zinc sulphide.
- 15 5. A formulation as claimed in any one of the preceding claims in which the THP⁺ salt comprises an anion selected from the group consisting of sulphate, chloride, phosphate, bromide, fluoride, carbonate, citrate, lactate, tartrate, borate, silicate, formate and acetate.
- 20 6. A formulation as claimed in any one of Claims 1 to 5 in which the thio-substituted compound is selected from the group consisting of thio-substituted carboxylic acids or salts; thio-substituted sulphonic acids; substituted and unsubstituted alkyl and aryl thiols; thio-substituted heterocyclic compounds; and mercaptoethanols.
- 25 7. A formulation as claimed in Claim 6 in which the thio-substituted compound is thioglycollic acid.
- 30 8. A formulation as claimed in any one of the preceding claims in which said formulation further includes a surfactant.

9. A formulation as claimed in Claim 8 in which the surfactant is a cationic surfactant.
- 5 10. A formulation as claimed in Claim 9 in which the cationic surfactant is selected from the group consisting of quaternary ammonium compounds, N-alkylated heterocyclic compounds, quaternised amido-amines, and amino methane phosphonate.
- 10 11. A formulation as claimed in Claim 8 in which the surfactant is selected from the group consisting of anionic, amphoteric and non-ionic surfactants.
- 15 12. The use of a formulation as claimed in any one of the preceding claims for treating corrosion of mild steel, copper or aluminium.
13. A method for treatment of an aqueous system containing or in contact with a metal sulphide scale while concomitantly inhibiting the corrosion of surfaces in contact with said aqueous system, which method 20 comprises the addition to said aqueous system of a scale and corrosion inhibiting amount of a formulation in accordance with any one of Claims 1 to 11.
14. A method according to Claim 13 in which the aqueous system is 25 used in enhanced oil recovery.
15. A method as claimed in Claim 13 in which the aqueous system is used in industrial water systems.
- 30 16. A method as claimed in Claim 13 in which the aqueous system is used in paper manufacturing systems.

17. A formulation consisting essentially of the reaction product of a THP⁺ salt (as hereinbefore defined) and a thio-substituted compound, wherein the ratio of said THP⁺ salt and said thio-substituted compound is
5 between 1:1 and 750:1.
18. A method as claimed in any one of Claims 13 to 16 in which the THP⁺ salt is added to the aqueous system in an effective amount of up to 30% by weight.
10
19. A formulation as claimed in any one of Claims 1 to 11 in which the ratio of the THP⁺ salt to the thio-substituted compound is between 1:1 and 750:1.
- 15 20. A formulation substantially as described herein with reference to the accompanying example.
21. A method substantially as described herein with reference to the accompanying example.
20

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB2004/001150

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C02F5/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 03/021031 A (BREEN STEVEN GERARD ; D ARBELOFF-WILSON SARAH (GB); DAVIS KEITH PHI) 13 March 2003 (2003-03-13) claims	1-21
X	WO 02/08127 A (FIDOE STEPHEN DAVID ; JONES CHRISTOPHER RAYMOND (GB); RHODIA CONS S) 31 January 2002 (2002-01-31) claims	1-4

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 May 2004	03/06/2004
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Serra, R

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No PCT/GB2004/001150

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
WO 03021031	A	13-03-2003	WO	03021031 A1		13-03-2003
WO 0208127	A	31-01-2002	AU	7080101 A		05-02-2002
			CA	2416465 A1		31-01-2002
			CN	1458907 T		26-11-2003
			DK	200300053 A		13-03-2003
			WO	0208127 A1		31-01-2002
			GB	2379440 A ,B		12-03-2003
			NO	20030230 A		12-03-2003
			US	2003226808 A1		11-12-2003